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Utilizing electrochemical impedance spectroscopy and neutron imaging to better understand transport characteristics of fuel cells

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Introduction

This project was essentially the basis of the Ph.D. dissertation of Dr. Douglas Aaron, who graduated from the Georgia Institute of Technology in August, 2010. The title of his dissertation was “Fuel cell transport studies: electrochemical impedance spectroscopy and neutron imaging”. The project was primarily focused on biofuel cells, a relatively new type of fuel cells utilizing bio-based materials and living organisms to catalyze fuel cell reactions. The benefits of biofuel cells include reduced cost, improved energy sustainability, and new applications for fuel cell technology. Two types of biofuel cells were the focus of this work: microbial fuel cells (MFCs) and enzyme fuel cells (EFCs). MFCs utilize living bacteria that exhibit exoelectrogenesis, a process by which microbes produce electricity while degrading carbon compounds. In an MFC, feed streams such as wastewaters or sugar solutions can be fed to the anode. The bacteria in the anode degrade the compounds while releasing electrons to an electrode. The cathode can consume the electrons produced by the bioanode, sustaining current flow. In an EFC, enzymes from living organisms are used to substitute precious metals, such as platinum, to catalyze fuel cell reactions. The inclusion of enzymes allows a variety of fuels to be utilized.

The primary obstacles to widespread implementation of biofuel cells are low power density and high cost. The high cost of biofuel cells is associated with the cost of materials relative to the low power density. In an effort to improve biofuel cell power density, studies utilizing electrochemical impedance spectroscopy (EIS) and neutron imaging have been employed to provide a better understanding of the transport processes occurring in the fuel cells. The effects of design and operation parameters for both MFCs and EFCs on internal resistances have been studied with EIS. Neutron imaging was utilized to study water loss in the enzyme-based cathode of EFCs in an effort to improve power density and longevity.

EIS Results

Experiments utilizing EIS to study transport resistances in MFCs have led to the conclusion that the current design that minimizes electrode spacing leads to a limiting step at the air-based cathode. We have optimized the bioanode such that its resistance is less than that of the cathode. It has also been observed that the cathode of the fuel cell responds more strongly to specific changes in anode operating parameters than the bioanode. One implication of this observation is that the different regions of the MFC (anode, solution, membrane, and cathode) are all interrelated and interdependent. In addition, the reaction occurring in the cathode (reduction of oxygen to water) can be limited by transport in other regions of the MFC. Figure 1 is a collection of Nyquist plots for EIS scans performed individually on the anode and cathode of the MFC, as well as a whole-cell scan between the anode and cathode. It is apparent that, for a mature MFC, the resistance measured in the bioanode is much smaller than that of the Pt-based air cathode. These measurements were made possible by inclusion of an Ag/AgCl reference electrode in the anode and cathode sections of the MFC. The solution resistance varied between the different EIS scans because of the inherently varying

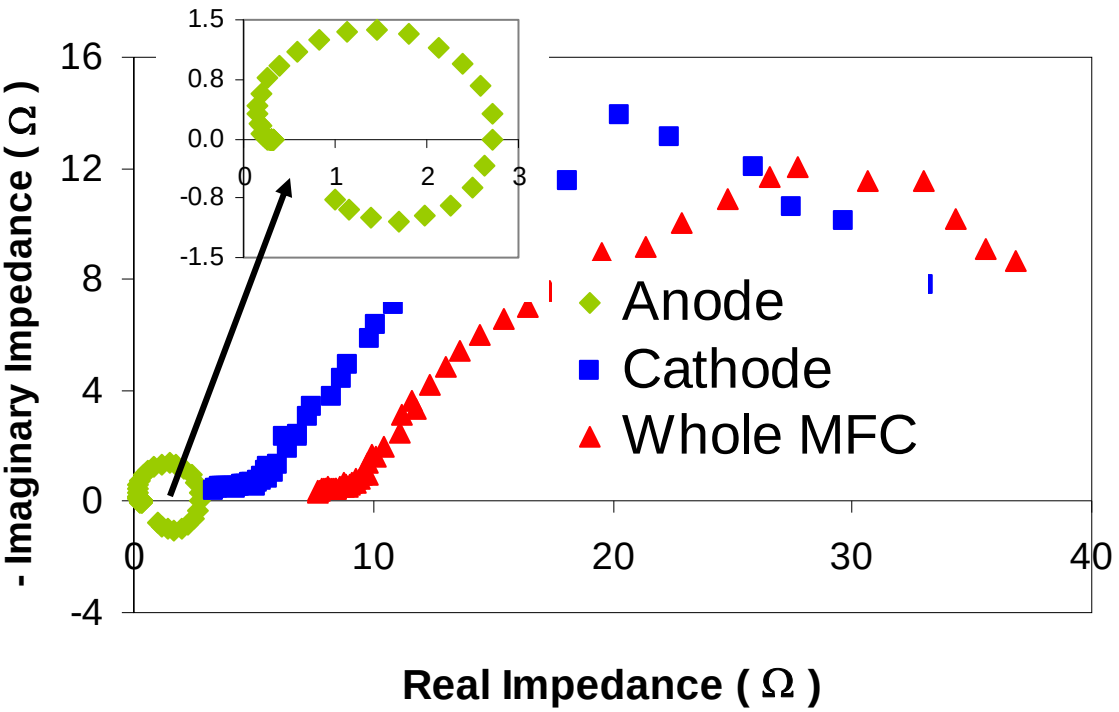
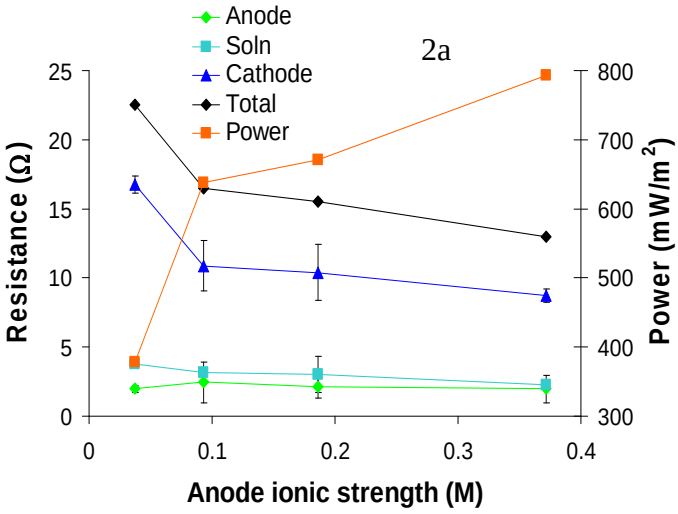


Figure 1. Nyquist plots for the anode, cathode and whole-cell MFC EIS measurements.

position of the working electrode with respect to the reference electrode.

Figure 2 shows that the cathode resistance responded more strongly to changes to the anode flow rate and ionic strength than did the bioanode. It can be seen in Figure 2a that the power output increased by a factor of two for a ten-fold increase in anode ionic strength. Over the same range, the cathode resistance decreased by approximately 35% while the anode resistance remained virtually unchanged. The solution resistance decreased slightly and the anode resistance was unchanged. In Figure 2b, it can be seen that a similar increase in power density, with reduction in cathode resistance, occurred when the anode flow rate was increased from stagnant to 24 mL/min.

It is believed that improved transport of protons from the anode to the cathode resulted from both increased ionic strength and increased anode flow rate. Increased ionic strength results in improved conductivity of the solution while increased anode flow rate provides convective transport of protons from the anode to the cathode (as opposed to just diffusion). With improved delivery of protons to the cathode, the reduction



of oxygen to water proceeds faster. The charge transfer resistance at an electrode is inversely proportional to the exchange current at that electrode. Since better proton transport would allow a greater reaction rate at the cathode, the resistance at the cathode decreased.

EIS was also used to study the EFC behavior over time. It has been observed that EFCs provide stable power for a short period of time and generally have very poor power output after one day of operation. Figure 3 shows EIS results for an EFC operating over two days. It can be seen that the cathode resistance dominated the total resistance throughout the experiment. The anode resistance increased slightly during the experiment, while the solution resistance was relatively stable. During the experiment shown in Figure 3, the power output of the EFC decreased by 95%.

The two mechanisms considered most likely to contribute to power loss and increased resistances for an EFC are water loss from the cathode and enzyme/mediator degradation. The air stream fed to the cathode was saturated, thus water loss was expected to be minimal. However, measurements of the carbon felt cathode suggested that significant water loss did occur during the experiment. This finding instigated neutron imaging of the EFC to quantify the water content and how it changed over time.

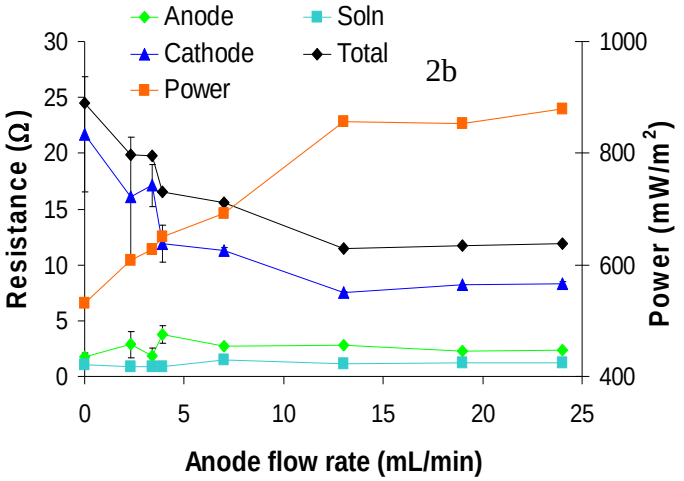


Figure 2. a) Effect of anode fluid ionic strength on power density and internal resistances. b) Effect of anode flow rate on power density and internal resistances.

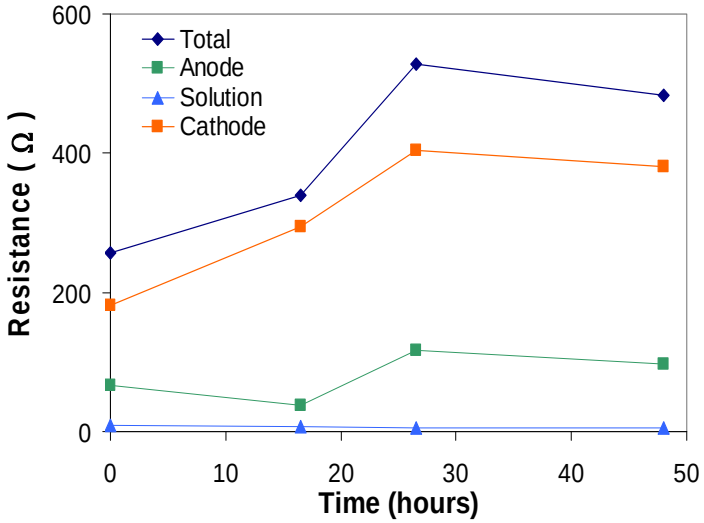


Figure 3. Profiles of internal resistances over time in the EFC measured via EIS.

Neutron Imaging Results

Water loss from the EFC cathode was observed in all experiments that were performed, even when 100% relative humidity (RH) air was fed to the cathode. It was hypothesized that the oxygen reduction reaction at the EFC cathode was exothermic; thus, it is possible that the cathode was heated up during the experiments. If this heating occurred, evaporation of water could account for the observed water loss. To test this hypothesis, neutron imaging was used to quantify the water loss rate of the EFC during multiple experiments. Mass and energy balances were performed on the EFC cathode

to test whether sufficient energy is given off during the production of water in the cathode to heat the humid cathode air stream as well as drive evaporation. Since the inlet conditions and the evaporation rate were known, mass and energy balances could be performed.

It was calculated that a temperature increase of approximately $0.4^{o}C$ could drive evaporation of water at the rate calculated via neutron imaging observations. Enough heat was generated in the EFC cathode to increase the temperature of the air stream by $0.4^{o}C$, thus local heating in the cathode can account for the observed water loss. This suggests that water loss may be inevitable from the EFC cathode as a result of the thermodynamics of operation. Neutron imaging of EFCs was performed for the first time in this study, and it may be used to optimize the performance of EFCs.

Is carbon capture and storage really necessary?

In addition to the EIS and neutron imaging work performed in this project, economic analysis of alternative energy technologies and carbon capture and storage (CCS) was performed. In this component of the project, the cost of CCS was compared with the cost of alternative energy technologies including wind, nuclear, and geothermal power. Based on a current emissions rate of 30 $GtCO_2$/year with an expected doubling time of 50 years, the most cost-effective method to reduce CO_2 emissions over time was calculated. "Virtual CCS (vCCS)" was considered to be the concept of redirecting the resources required to perform CCS on CO_2 emissions to developing alternative energy. The alternative energy installations were considered to have avoided CO_2 emissions based on how much CO_2 is given off during the combustion of coal to produce electricity. Estimates of the cost for CCS, wind power, nuclear power, geothermal power, and CO_2 emissions rates were obtained from the literature including the IPCC *Special Report on Carbon Dioxide Capture and Storage*, the Energy Information Administration, and reports from U.S. national laboratories.

On an economic basis, it was found that all three alternative energy technologies are much more cost-efficient for avoiding CO_2 emissions from power production. Wind power, nuclear power, and geothermal power were 190%, 430%, and 450% more efficient than CCS. In addition to avoiding much more CO_2 per dollar, each of these alternative energy technologies produced valuable electricity that could be sold to earn a profit. CCS, on the other hand, is expected to have no valuable return. In addition, the environmental and socio-political obstacles associated with CCS caused us to conclude that vCCS is a much more responsible and promising method to stabilize CO_2 emissions at the present rate. The results of this study have been included in a Viewpoint article published in the journal Environmental Science & Technology and highlighted on the cover of the June 1 issue of the journal.

Publications

A list of publications that include the results of this study is provided in the Appendix.

Appendix: Publications Produced by this Project

Peer-Reviewed Publications

Aaron, D.S. Fuel cell transport studies: electrochemical impedance spectroscopy and neutron imaging. Ph.D. Dissertation, Georgia Institute of Technology, **2010**.

Aaron, D.S.; Tsouris, C.; Hamilton, C.Y.; Borole, A.P. Assessment of the Effects of Flow Rate and Ionic Strength on the Performance of an Air-Cathode Microbial Fuel Cell Using Electrochemical Impedance Spectroscopy. Energies **2010**, 3, 592-606.

Tsouris, C., Aaron, D.S., Williams, K.A. Is carbon capture and storage really necessary? Environmental Science and Technology, **2010**, 44(11), 4042 – 4045.

Borole, A.P.; Aaron, D.S.; Hamilton, C.Y.; Tsouris, C. (2010). Understanding Long-term Changes in Microbial Fuel Cell Performance Using Electrochemical Impedance Spectroscopy. Enviromental Science and Technology, **2010**, 44(7), 2740 – 2745.

Borole, A.P.; Hamilton, C.Y.; Aaron, D.S.; Tsouris, C. Investigating microbial fuel cell bioanode performance under different cathode conditions. Biotechnology Progress, **2009**, 25(6): 1630 - 1636.

Aaron, D.S.; Borole, A.P.; Hussey, D.S.; Jacobson, D.L.; Yiacoumi, S.; Tsouris, C. Quantifying the water content in the cathode of enzyme fuel cells via neutron imaging. Journal of Power Sources, in review, **2010**.

Aaron, D.S.; Borole, A.P.; Yiacoumi, S.; Tsouris, C. Effects of Operating Conditions on Internal Resistances in Enzyme Fuel Cells Studied with Electrochemical Impedance Spectroscopy. Electrochimica Acta, in preparation, **2010**.

Presentations

Aaron, D., A. P. Borole, C. Y. Hamilton, C. Tsouris. “Understanding long-term changes in microbial fuel cell internal resistance using electrochemical impedance spectroscopy.” Annual AIChE Meeting, Nashville, TN, November, 2009.

Aaron, D., A. P. Borole, D. Jacobson, D. Hussey, S. Yiacoumi, C. Tsouris. “Neutron imaging of an enzyme fuel cell.” Annual AIChE Meeting, Nashville, TN, November, 2009.

Aaron, D., A. P. Borole, D. Jacobson, D. Hussey, S. Yiacoumi, C. Tsouris. “Transport properties of enzyme fuel cells studied by electrochemical impedance spectroscopy and neutron imaging.” 16th Syposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October, 2009.

Borole, A.P., S. LaBarge, B. Spott, D.S. Aaron, C. Tsouris, D. Hussey, and D. Jacobson, “Enhancing Performance of Enzyme Fuel Cells via the Use of Gas-Phase Reagents,” 2009 ACS Meeting, August, 2009.

Aaron, D., A. P. Borole, D. Jacobson, D. Hussey, S. Yiacoumi, C. Tsouris. “Electrochemical impedance spectroscopy and neutron imaging investigations of enzyme fuel cells.” 83rd ACS Colloid and Surface Sciences Symposium, American Chemical Society, New York, NY, 2009.